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Title: Molecular-dynamics simulation of the growth of diamondlike films by energetic carbon-atom beams

Year: 1992

Version: Final published version

Please cite the original version:

Kaukonen, H.-P. & Nieminen, Risto M. 1992. Molecular-dynamics simulation of the growth of diamondlike films by energetic carbon-atom beams. Physical Review Letters. Volume 68, Issue 5. 620-623. ISSN 0031-9007 (printed). DOI: 10.1103/physrevlett.68.620.

Molecular-Dynamics Simulation of the Growth of Diamondlike Films by Energetic Carbon-Atom Beams

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(Received 23 May 1991)

The growth of diamondlike films and overlayers by the deposition of energetic carbon atoms has been investigated by molecular-dynamics simulations. The interatomic many-atom potential suggested by Tersoff is used. The structural analysis of the grown films shows that there is an energy window between 40 and 70 eV for the deposited atoms where the growth most closely results in a dense diamondlike structure. This observation supports earlier experimental suggestions for optimal deposition conditions.

PACS numbers: 68.55.−a, 81.15.−z

Considerable effort has been devoted to the development of methods to synthesize diamond and diamondlike films and coatings at low temperature and pressure, motivated by the unique characteristics of diamond. Deposition of films exhibiting diamondlike properties has been demonstrated with various methods: chemical vapor deposition (CVD) [1], rf and dc plasma deposition [2], laser plasma source method [3], mass-separated ion-beam deposition [4], and sputtering techniques [5]. Ion-beam deposition occurs usually at around 300 K whereas CVD methods require substantially higher temperatures.

In contrast to (micro)crystalline diamond films (DF) consisting of purely fourfold-coordinated sp^3-bonded carbon atoms, the diamondlike films (DLF) obtained by ion bombardment (*i*-C) are strikingly disordered, showing a mixture of sp^2 and sp^3 bonding [2(a)–2(c),3,4(a),4(d)]. The diamondlike features are usually attributed to the extent of sp^3 hybridization present in the material.

In most studies hydrocarbon ions or reactants have been used, the properties of the film varying with the hydrogen content. Pure carbon films are usually harder and more wear resistant [4(b),4(c)], transparent, and their density is closer to that of crystalline diamond [2(b), 4(a),4(c),4(d)].

The physical properties of ion-beam-deposited (*i*-C) diamondlike films, such as density, hardness, wear resistance, electrical resistivity, and optical transparency, are strongly interrelated. Using atomic-beam techniques, the optimal values are invariably obtained within an energy interval of incident particles which is practically the same for all parameters typical of diamondlike qualities. This reported energy window depends on the applied method and deposition conditions. Some of the values reported in the literature are E_{beam}=40–80 eV [2(b)], 115–215 eV [4(d)], and 100–500 eV [4(c)].

In this paper we present atomistic molecular-dynamics (MD) simulations of the growth of diamondlike films using a realistic many-body potential [6] for carbon. We study at the microscopic level the energy dependence of the quality of the growing film using a monoenergetic beam of neutral carbon atoms. The many-body potential is used to describe the collisions between the atoms as well as the structural relaxations and annealing. The inelastic processes due to electronic excitations are not important in the energy range studied and thus the electronic stopping power is neglected. We also focus on neutral carbon atoms; the true charge state is important for the first few collisions only. The energy range of interest is limited to below 100–200 eV. Our purpose is not to simulate any particular experiment but instead to isolate the part that interatomic collisions and subsequent relaxations play in the growth process.

As the substrate we employ an ideal diamond (100) film consisting of twelve atomic layers with 32 atoms each, i.e., a total of N=384 substrate atoms. The two bottom layers are fixed to their equilibrium positions representing a semi-infinite crystal. The remaining ten layers are allowed to move with full dynamics. In all simulations the carbon-carbon interactions are described via the empirical classical many-body potential proposed by Tersoff [6]. The parameters of the potential are obtained from a fit to the cohesive energies of carbon polytypes and to the lattice constant and bulk modulus of diamond. The bond lengths and cohesive energies of a large variety of carbon types ranging from the C_2 dimer to closed-packed metallic structures are well described. Phonon energies and elastic constants and the energies of a number of diamond defects also compare well with experiments. The potential gives a rather satisfactory overall description of carbon in different bonding environments and thus one expects it to be reasonably accurate in describing the simulation of disordered carbon films.

The atomic beam growth of carbon coatings was studied using five different beam energies, E_{beam}=1, 10, 25, 40, and 70 eV. In addition, particles with energy 150 eV were shot into the film grown with E_{beam}=40 eV to study the possible deteriorating effect of higher-energy particles on the film.

The substrate was allowed to relax at T=300 K and P=0 for 2000Δt, with Δt=0.5 fs, employing the method of Berendsen *et al.* [7] to simulate the canonical (N,T,P) ensemble. This algorithm is especially suitable for nonequilibrium molecular dynamics since local disturbances are kept to a minimum while preserving global gradients.

TABLE I. Time interval N_t, time step Δt, and coordination numbers Q_n vs beam energy. The cutoff in the bond-angle determination used was $r_c = 1.97$ Å.

E (eV)	N_t	Δt (fs)	Q_2	Q_3	Q_4	Q_5
1	500	0.5	0.190	0.732	0.067	0.000
10	600	0.4	0.029	0.664	0.307	0.000
25	700	0.35	0.054	0.606	0.340	0.000
40	780	0.32	0.024	0.525	0.438	0.013
70	1000	0.25	0.029	0.606	0.361	0.004
150	1500	0.17	0.053	0.591	0.351	0.005

Therefore the method applies well to the cooling of the system in the growth phase (see below). Dynamical properties are not significantly altered if the relaxation time constants of volume and temperature τ_P and τ_T are chosen large enough.

During the growth phase the dimensions of the simulation cell were kept fixed in the lateral x and y directions (i.e., $\tau_P = \infty$). Layers of carbon film were grown atom by atom onto the film by shooting particles with fixed beam energy E_{beam} perpendicular to the surface at a random position in the x-y plane. The number of time steps N_t between injected atoms was chosen large enough so that the previous atom had enough time to dissipate its energy to the substrate before the next atom hit the surface. The particle (and energy) flux dictated by the computer limitations (one slowing-down trajectory of a carbon atom requires 200–900 s on a CRAY X-MP/432) is naturally much larger than in real experiments. This can lead to detrimental heating of the surface region. In order to avoid this we used a method introduced by Luedtke and Landman [8] in which only the last $N_d = 10$ particles are followed with full dynamics. The velocities of the rest of the surface atoms are periodically scaled down to obtain the required substrate temperature T_0. In this scaling we applied the Berendsen method. Velocities were scaled every $4\Delta t$ on the average with $\tau_T/\Delta t = 50$. The velocity scaling factor λ was greater than 0.992 even with $E_{\text{beam}} = 150$ eV. The time interval N_t between two beam particles and the time steps used with different beam energies are shown in Table I. For each beam energy a total of approximately 320 atoms were grown onto the surface corresponding to ten layers of ideal substrate.

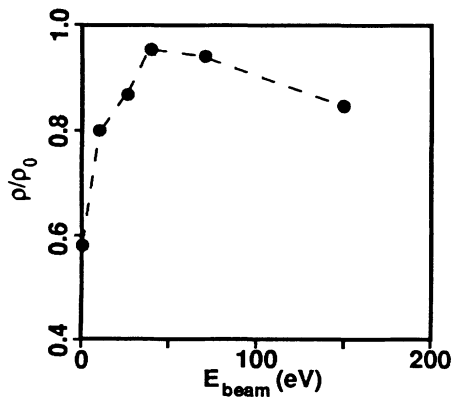

FIG. 1. Fractional density ρ/ρ_0 of the grown film vs beam energy (ρ_0 is the density of bulk diamond); energy in eV.

After growth the layers were allowed to relax for 5–10 ps, keeping the simulation cell constant. Finally, full structural analysis was performed for the relaxed layers.

The density of the films was determined by cutting a slice in the z direction, moving this slice in small increments across the film, and finally averaging over the section in the z direction where the density profile remained roughly constant. A few outermost layers, corresponding at least to the penetration depth of incident particles, evident from the structure factor

$$S_{\mathbf{q}} = \left| \frac{1}{N} \sum_i e^{i\mathbf{q}\cdot\mathbf{r}_i} \right|^2 , \tag{1}$$

were excluded in order to minimize surface effects. [The structure factor was determined for $\mathbf{q} = (2\pi/a)(1,1,0)$ for each section of the film corresponding to a full layer spacing in the z direction.] The density ρ of the film as a function of beam energy is shown in Fig. 1. One finds that the largest density $\rho/\rho_0 = 0.95$ (ρ_0 is the density of bulk diamond) is obtained for films grown with energies between 40 and 70 eV and that the bombardment of particles with energy 150 eV leads to a significant decrease of the density.

Table I shows the distribution of coordination numbers Q_n, determined using the position of the first minimum of the pair correlation function $g(r)$ as the cutoff radius for bond counting. The fraction of fourfold-coordinated (sp^3 bonded) atoms is largest in the 40- and 70-eV films, reaching a maximum of 44% in the 40-eV film. The 1-eV film has 19% sp^1-, 73% sp^2-, and only 7% sp^3-bonded atoms, which is in qualitative accordance with the experimental observations of coordination of amorphous carbon films obtained with low particle energies [2(c),3], the recent *ab initio* molecular-dynamics study by Galli *et al.* [9], and the calculations by Robertson and O'Reilly [10]; the fraction of sp^1 bonding is, however, significantly larger in the beam-deposited material.

The ring statistics for the films is shown in Table II. The 1-eV sample contains a large number of rings, larger than the nine atoms typical of a chainlike porous structure, consistent with the low density observed. The small fraction of six rings indicates the lack of medium-range "graphitic" order in the film. As the energy is increased the amount of five, six, and seven rings typical of a fourfold amorphous structure grows, reaching a peak in the 40-eV sample. At the same time the fraction of large rings decreases. Again, one finds a destructive effect of the 150-eV particles on the grown layer.

The pair correlation function $g(r)$ is shown in Fig. 2(a). For the 1-eV beam the structure is very similar to

TABLE II. Ring statistical analysis. A ring is defined as the shortest connective path between two bonds originating from a given atom. Entries are given per atom.

E (eV)	5	6	7	8	9	>9
1	0.01	0.51	0.66	0.44	0.18	0.99
10	0.38	1.05	1.18	0.67	0.32	0.27
25	0.28	1.23	1.03	0.76	0.33	0.26
40	0.56	1.47	1.33	0.66	0.25	0.09
70	0.41	1.13	1.19	0.79	0.39	0.16
150	0.38	1.24	0.86	0.78	0.54	0.18

those obtained by previous *ab initio* MD [9] and Monte Carlo studies of amorphous carbon [6(a)]. The first- and second-neighbor peaks are sharp. As the energy is increased the first-neighbor peak spreads as the fraction of sp^3 bonding grows. The second-neighbor peak broadens also and an additional feature typical of glassy materials begins to emerge on the left side. Figure 2(b) shows the partial correlation functions g_{ij} $(i,j=3,4)$, where i and j denote coordination numbers, for the 1- and 40-eV films. The additional feature in the second-neighbor peak is clearly explained by the peak in g_{33} of the 40-eV film (absent in the 1-eV film). This peak corresponds to a second-neighbor distance between two threefold-coordinated atoms connected by a bond angle of approximately 90°. There is an increase in the small-angle part of the bond-angle distribution function $A_4(\theta)$ for fourfold-coordinated atoms in films grown with larger energies, suggesting that the connecting atom is predominantly fourfold coordinated, and also indicating a tendency for the formation of sp^2-sp^3-sp^2 chains. The atoms with different bonding are fairly randomly distributed (i.e., there is only little clustering in the 40-eV layer), as seen from the ratio $\int_{nn} r^2 g_{43}(r)dr / \int_{nn} r^2 g_{44}(r)dr = 1.1$ (nn means integration over the first peak only) when compared to $Q_3/Q_4 = 1.2$ for a random distribution. The final structures of the two layers grown with 1 and 40 eV are shown in Fig. 3. The porous structure of the low-energy film and the very dense disordered structure of the 40-eV film are apparent.

Analysis of the vibrational (phonon) density of states was also carried out to the 1- and 40-eV layers. There is a slight shift to lower frequencies as the density of the film decreases, consistent with the onset of low-frequency "interlayer graphitic" modes associated with sp^2 bonding.

Earlier, related work for Si [11] and C [12] has focused on individual trajectories of impinging atoms and their effect on the stress distribution in the substrate. This is the first study of the actual structure of the growing film.

In summary, we have shown that classical simulations of the initial stage of the growth process of diamondlike films using energetic neutral carbon atoms reproduce the trend observed in experiments [2(b),4(c),4(d)] exhibiting

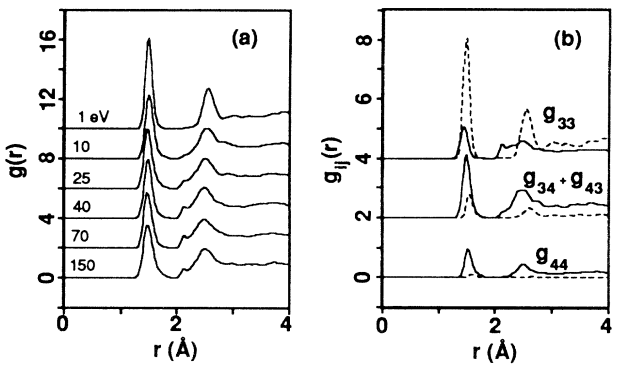

FIG. 2. (a) Pair correlation function $g(r)$ for the films grown with $E_{beam}=1$, 10, 25, 40, and 70 eV and the film obtained by shooting 125 particles with energy $E_{beam}=150$ eV on the 40-eV film. Note the emergence of the shoulder in the second-neighbor peak with increasing beam energy. (b) Pair correlation function $g_{ij}(r)$ of atoms with coordination numbers $(i,j)=3,4$ for the films grown with $E_{beam}=1$ and 40 eV. The dashed and solid lines correspond to the 1- and 40-eV films, respectively. Note the peak in $g_{33}(r)$ for $E_{beam}=40$ eV. $g(r)=\sum_i g_{ii}(r)+\sum_{i\neq j} g_{ij}(r)$.

an energy window ($E_{beam}=40$–70 eV) which leads to optimal growth. The film obtained with low energies consists of an amorphous, mostly sp^2-bonded, porous structure which compares well with experimental [2(c),3] and theoretical [6(a),9,10] observations. At higher energies one obtains a strongly disordered structure with a large fraction of sp^3 bonding and a density close to bulk diamond. The simulations suggest that a description neglecting inelastic (electronic) processes is adequate in

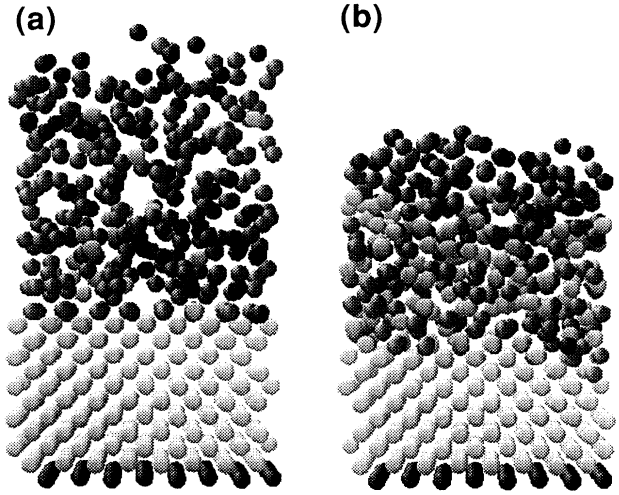

FIG. 3. Snapshots of the two films grown with (a) $E_{beam}=1$ and (b) $E_{beam}=40$ eV after growth and relaxation of 7 ps. The black, grey, and white spheres correspond to twofold-, threefold-, and fourfold-coordinated atoms, respectively. The total number of atoms is $N=678$ (a) and $N=674$ (b).

explaining the observed behavior as a function of beam energy and thus contains the essential physics of the system. The optimal energy region results from the interplay between annealing due to local heating and damage production, both induced by the energetic atoms during growth. Beam energies lower than a few eV lead to an amorphous, mostly sp^2-bonded amorphous structure exhibiting a small optical gap and low density. Increasing the beam energy leads to the collapse and densification of these porous structures. At high energies the incident ion causes a thermal spike, producing local defects in the growing film. Unless the temperature of the substrate is increased the high thermal conductivity of diamond prevents the annealing of these defects and the nucleation of sp^3 bonds.

We wish to thank Dr. A. Anttila and Dr. W. D. Luedtke for many useful discussions. Financial support of the Foundation of Neste Corporation, The Finnish Academy of Sciences, and the Wihuri Foundation is gratefully acknowledged. The computations were performed at the Finnish Center of Scientific Computing and at the National Energy Research Supercomputer Center, Livermore, California through Grant No. FG05-86ER45234 by the U.S. Department of Energy. Part of this work was done during a visit (H.-P.K.) to the School of Physics at Georgia Institute of Technology.

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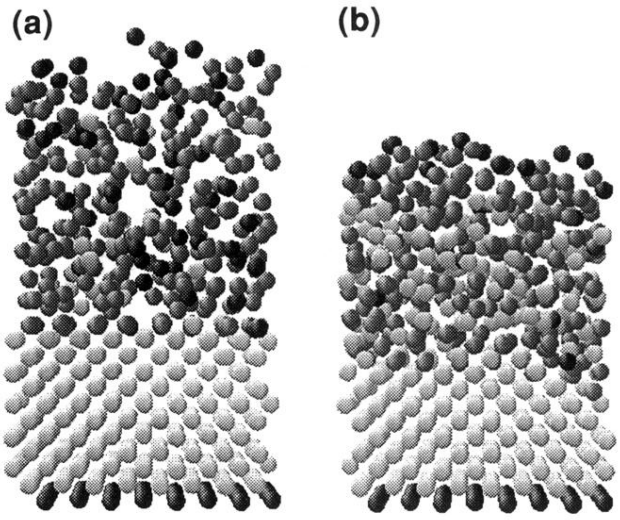

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